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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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Additional inventors are being named on the _____ 2nd _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
ARYL METHYLSILYLS USED AS FLAME RETARDANT ADDITIVES					
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
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[Page 1 of 2]

Respectfully submitted,

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(if appropriate)

Docket Number: ACA 6235 PRUS

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Docket Number **ACA 6235 PRUS**

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ARYL METHYLSILYLS USED AS FLAME RETARDANT ADDITIVESBackground of the Invention

5 Due to having excellent mechanical, electrical and thermal properties, molded parts comprising aromatic polycarbonate resins have been commonly used as engineering plastics in a wide variety of applications including business
10 machines, electric and electronic devices, automotive parts, and in building fields components. To overcome the drawbacks of aromatic polycarbonate resins in regard to their processability and moldability, a number of polymer blends with other thermoplastic resins, such as polystyrene resins,
15 acrylonitrile-butadiene-styrene (ABS) resins, and polyester resins, have been developed. Among others, the polymer alloys comprising an ABS resin have been widely used in the automobile, business machine and electric and electronic fields.

20 In current end use applications, including for business machines, electric appliances and the like, it is strongly desired to have the resin materials flame retardant. To meet this requirement, numerous flame retarding techniques have been proposed for aromatic polycarbonate resins and its
25 polymer alloys with other thermoplastic resins.

It was, for example, a common practice to use an organic halide flame retardant containing bromine in combination with a flame retardant aid such as antimony trioxide as disclosed in U.S. Patent No. 6,043,310. Resin compositions of this
30 formulation are made flame retardant to a relatively large extent, but raise environmental problems in giving off harmful or toxic substances upon disposal by incineration. In

addition, the production of molded parts from such resin compositions has the disadvantage that, if thermally decomposed, the flame retardant gives off hydrogen halide which can cause corrosion of the molds used in the manufacturing process or detract from the physical properties of molded resin parts themselves. For this reason, efforts have been made to achieve flame retardancy without resorting to organic halide compounds containing bromine.

For example, attempts have been made to use oligomeric phosphate esters in combination with polytetrafluoroethylene, which has a fibrillating ability. Aromatic bisphosphates have characteristics such as low volatility, high temperature stability and low tendency to exude the polymer, so that they are used as a flame retardant or plasticizer for imparting fire retardancy, temperature stability and good moldability to thermoplastic resin. Also, aromatic bisphosphates show resistance to high temperature up to 300°C, which is necessary for processing of some engineering plastics.

However, the long-term heat and hydrolytic stability of PC/ABS flame retarded with aromatic bisphosphates is not always satisfactory. Furthermore, aromatic phosphates tend to decrease the dimensional stability of the resin at elevated temperatures.

By contrast, silicone resins have high heat resistance, give off no toxic gases upon combustion, and are safe in themselves. Silicone resins of several types have been proposed as the flame retardant for polycarbonate resins. In fact, silicone resins are used as the flame retardant in resin compositions of which business machine parts are made.

U.S. Patent Nos. 5,955,542; 6,001,921; and 6,184,312; and European Patent Application No. 1,094,093; 1,272,565; and 1,293,551 all describe flame retarded resin compositions containing silicone resins comprising di- and trifunctional siloxane units, having a relatively high molecular weight and bearing phenyl groups. Allegedly, these silicone resins, which have branched structures, offer improved heat resistance, and the silicone resins bearing phenyl groups exert flame retardant effects by forming an incombustible Si-C ceramic layer through mutual coupling of aromatic rings on the surface of the resin to which it is added.

Also, U.S. Patent Nos. 6,326,425 and 6,509,421 describe a thermoplastic resin composition comprising an aromatic polycarbonate resin and a methyl-phenyl or isopropyl-phenyl silicone oligomer. PCT Patent Application No. WO 99/28387 describes a flame retardant polycarbonate resin composition comprising, as essential components an aromatic polycarbonate resin, a branched organic silicone and an alkali metal salt of perfluoroalkanesulfonic acid. European Patent No. 1,277,799 describes a flame retardant polycarbonate resin composition comprising branched a methyl-phenyl siloxane in combination with potassium perfluorobutane sulfonate or the potassium salt of diphenylsulfonic acid. Similar, the use of a branched methyl-phenyl siloxane, either in combination with polytetrafluoroethylene or sodium trichlorobenzenesulfonate (U.S. Patent No. 6,534,576) or in combination with sodium chloride (European Patent Application EP 1,302,510) has also been described.

The use of linear poly(methylsiloxans) or poly(methylphenylsiloxanes) in polycarbonate compositions is described in

U.S. Patent Nos. 6,541,548; 6,451,906 and 6,454,969. PCT Patent Application No. WO 02/46288 describes a flame retarded polycarbonate resin composition comprising a poly(methyl-phenylsiloxane) in combination with bisphenol A bis(diphenyl phosphate) , and PCT Patent Application WO No. 02/081566 and European Patent Application No. 1,342,753 describe similar compositions but in combination with potassium perfluorobutane sulphonate or diphenylsulfon-3 sulfonate. The use of cyclic octaphenylcyclotetrasiloxane is described in European Patent Application No. 1,278,798 and in U.S. Patent No. 6,541,548. Copolymers of linear polysiloxanes with polycarbonate resin, which provide flame retardant performance, are described in U.S. Patent Nos. 6,323,280 and 6,576,706 and in PCT Patent Application Nos. WO 03/008501 and WO 03/042305.

By using transmission electron microscopy, it was shown in European Patent Application No. 1,272,565 that in molded parts siloxane moieties are mostly distributed near the surface of the part. It is believed that when these resin compositions are burned, organopolysiloxane molecules or an organopolysiloxane and a resin component are joined through oxidative decomposition and crosslinking of alkoxy or organooxy groups, to form a network structure which is fixed in proximity to the burning portion, thus exerting flame retardant effects.

One aspect of the present invention is to provide a flame retarded resin composition comprising an aromatic polycarbonate resin that is flame retardant and safe and that imposes minimal environmental loads, thereby obviating or eliminating the use of organic halogen flame retardants, which give rise to environmental and manufacturing problems and to

the use of phosphate flame retardants, which give rise to problems of lowering heat resistance as earlier mentioned.

It has been found that a resin composition comprising an aromatic polycarbonate resin will be endowed with flame retardance and anti-dripping properties by compounding the resin with an oligomeric aryl methylsilyl having silicon atom-bonded methyl groups and phenyl and phenylene groups that are bonded via Si-O bonds.

10 Detailed Description of the Invention

In the flame retarded resin composition of the present invention, any aromatic polycarbonate resin may serve as component (A) as long as molded parts can be formed therefrom. This polycarbonate resin substrate can be any polycarbonate resin known in the art. The aromatic polycarbonates that are the main constituent of the invention are generally prepared by reacting a diphenol compound with phosgene and generally have an average molecular weight of from about 10,000 to about 200,000.

20 In the flame retarded composition of the invention, another thermoplastic resin may be included in component (A) along with the aromatic polycarbonate resin. Typical examples of other thermoplastic resin components that may be present include polystyrene, acrylonitrile-butadiene-styrene (ABS), polyester, and polyamide s, as well as polyethylene, polypropylene, polybutene, polysulfone, polyvinyl acetate, ethylene-vinyl acetate copolymers, poly(methyl methacrylate), polyethylene oxide, cellulose acetate and cellulose nitrate. Of these thermoplastic resins, ABS resins are preferred since
30 they are customarily used as polymer alloys with aromatic

polycarbonate resins. The thermoplastic resins may be used alone or as mixtures of two or more with the polycarbonate.

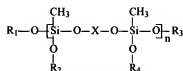
Polystyrene resins that can be used are polymers produced through polymerization of unsaturated monomers containing
5 aromatic vinyl monomers. Such polymers modified with rubbery polymers are also included.

ABS resins that can be used are graft polymers produced through graft polymerization of vinyl monomers containing aromatic vinyl monomers with rubbery polymers. Mixtures of
10 polymers produced through polymerization of vinyl monomers containing aromatic vinyl monomers and the graft polymers are also useful. The graft polymers are produced by graft polymerizing an aromatic vinyl monomer and one or more monomers selected from (meth)acrylonitrile, (meth)acrylates,
15 maleimide monomers and unsaturated dicarboxylic acid anhydride monomers with rubbery polymers having a glass transition temperature of 10°C or lower.

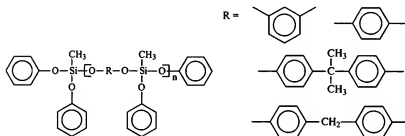
As component (A) in the flame retarded resin composition of the invention, the aromatic polycarbonate resin may be used
20 alone or in admixture with a thermoplastic resin other than the aromatic polycarbonate resin, as mentioned above. The blend proportion of the aromatic polycarbonate resin to the other thermoplastic resin can be in the range from 10/90 to 100/0 by weight. In order that the resin composition maintains
25 satisfactory levels of flame retardance, impact resistance, processing and molding, the blend proportion of polycarbonate should preferably be at least 30/70, more preferably at least 50/50 by weight.

Component (B) in the flame retardant resin composition of
30 the invention is an aryl methylsilyl containing methyl groups

attached to the silicon atoms in a molecule, having ph noxy groups, having phenylene bridging groups and having the following formula:



- 5 where R_1 , R_2 , R_3 , R_4 are each independently aryl or substituted aryl, X is a bridging group derived from a diol that comprises an arylene moiety and n can range from about 1 to about 20. The grouping -O-X-O- can be derived from such diols as hydroquinone, resorcinol, and bisphenol A.
- 10 The most preferable aryl methylsilyls for use in accordance with the present invention are shown in the following formula:



- 15 The foregoing class of flame retardant additive can be made by reacting an alkytrichlosilane with phenol or a substituted phenol followed by reaction with diphenol. Suitable diphenols include hydroquinone, resorcinol, bisphenol A, bisphenol F, and bisphenol S. Depending on the ratio of
- 20 phenol to diphenol, different molecular weight oligomers can be synthesized. Unreacted and partially reacted species can be removed from the reaction mixture by distillation.

When phenoxy groups are incorporated in such silyl compounds, transesterification and crosslinking with the

polycarbonate take place during combustion to form a flame retarded layer in proximity to the burnt portion, thus preventing flaming particles from dripping.

5 In addition to the aforementioned components, other
customary additives may be added to the flame retarded resin
composition of the invention during the kneading or molding
step to achieve desired enhanced physical properties for the
final composition, insofar as they do not compromise the
physical properties of that composition. Exemplary additives
10 include colorants, fillers, stabilizers, elastomers, other
than the thermoplastic resin used as component (A),
reinforcements (e.g., carbon fibers), UV absorbers,
lubricants, mold release agents, plasticizers, flow modifiers,
antistatic agents, and dispersants.

15 In preparing the flame retardant resin composition of the
invention, any conventional method may be employed. Most
often, the composition is prepared by first combining
components (A) and (B), further combining any desired optional
components and other additives, and mixing the resulting
20 composition. The order of mixing these components is not
critical. Using well-known molding techniques, the flame
retarded resin composition thus obtained can be molded into a
variety of molded parts, typically electric appliance parts.

Examples

Preparation Examples, Examples and Comparative Examples are given below for further illustrating the present invention. These Examples are not to be construed as limiting the scope of the invention since they are given to merely illustrate certain embodiments that can be formulated.

Example 1

First, 50g (0.33mol) of methyltrichlorosilane was added in droplet form with continuous stirring to 62.8g (0.66mol) of phenol over a five minute period at the room temperature under a continuous flow of dry nitrogen. The reaction mixture was heated up to 75°C. After two hours of stirring at this temperature, the reaction mixture was heated up to 150-170°C and was stirred for two hours. After cooling, 18.4g (0.167mol) of hydroquinone was added to the mixture. Then, the reaction mixture was heated to 75-100°C. After one hour of stirring at this temperature, the reaction mixture was heated to 150-200°C and was stirred for three hours. Unreacted substances were then removed by distillation under vacuum at 170 °C/15mm. The residue was a viscous light-brown liquid that contained of dimer and oligomeric materials. This mixture of products was separated by distillation under vacuum. The dimer (Dimer 1) was a colorless liquid, which had a boiling temperature of 230-240°C/15mm. The yield of dimer is 25%. The oligomer (Oligomer 1) was a light-yellow jelly-like mass. The yield of oligomer was 50%. The measured content of Si in dimer is 8.98% and was 11.5% in oligomer.

Example 2

First, 50g (0.33mol) of methyltrichlorosilane was added in droplet form with continuous stirring to 62.8g (0.66mol) of phenol over a five minute period at room temperature under a continuous flow of dry nitrogen. The reaction mixture was then heated to 75°C. After two hours of stirring at this temperature, it was heated to 150-170°C and was stirred for an additional two hours. After cooling, 18.4g (0.167mol) resorcinol was then added. Then the reaction mixture was heated to 75-100°C. After one hour of stirring at this temperature, the reaction mixture was heated to 150-200°C and was stirred for an additional three hours. Unreacted substances were then removed by distillation under vacuum at 170-175 C/15mm. The residue appeared as a viscous light-brown liquid. A mixture of products was separated by distillation under vacuum. A dDimer (Dimer 2) was a colorless liquid, which had boiling temperature 220-230 C/15mm. The yield of dimer is 27%. An oligomer (Oligomer 2) was isolated as a yellow jelly mass. The yield of this oligomer was 53%. The measured content of Si in the dimer was 8.46% and was 10.0% in oligomer .

Example 3

First, 100g (0.66mol) of methyltrichlorosilane was added as droplets with continuous stirring to 125.6 g (1.32mol) of phenol over a five minute period at room temperature under a continuous flow of dry nitrogen. The reaction mixture was heated to 70-75°C. After two hours of stirring at this temperature, it was then heated to 170°C and was stirred for an additional four hours. After cooling, 68g (0.34mol) of 4,4'-methylenediphenol was then added. Then the reaction mixture was heated to 170°C and was stirred for four hours. Non-reacted substances were removed by distillation under vacuum at 170°C/15mm. The residue was a light-yellow jelly mass (Oligomer 3). Its yield was 73%.

15

Example 4

First, 50g (0.33mol) of methyltrichlorosilane was added in droplet for with continuous stirring to 62.8g (0.66mol) of phenol over five minutes at room temperature under a continuous flow of dry nitrogen. The reaction mixture was heated to 75°C. After two hours of stirring at this temperature, it was heated to 170°C and was stirred for an additional four hours. After cooling, 38g (0.17mol) of 4,4'-isopropylenediphenol was added. Then the reaction mixture was heated to 170°C and was stirred for an additional four hours. Non-reacted substances were removed by distillation under vacuum at 170°C/15mm. The residue was a viscous light-brown liquid. This mixture of products was separated by distillation under vacuum. A dimer (Dimer 4) component, which was a colorless liquid, having boiling temperature of 210-235°C/15mm, was isolated. The yield of dimer was 23%. An oligomer (Oligomer 4), which was a light brown jelly mass, was also isolated. The yield of this oligomer was 57%.

20

Example 5

In this Example, 40 g of polycarbonate resin, 8 g of ABS resin, and 12 g of the flame retardant additives from each of

5 Examples 1-4 were melt blended in a bowl-type mixer at 250°C over a period of five minutes. The resulting flame retarded compositions were then compression molded into slabs (3.0 mm thickness). Specimens (3.0 x 6.0 x 120mm in size) for

10 flammability tests were then cut from the slabs. The flammability of these PC/ABS formulations was then evaluated by the Limiting Oxygen Index (LOI) test (ASTM D 2863). The results are shown in Table 1:

Table 1

#	Aryl methylsilyl	LOI
1	None	23.4
2	Dimer 1	24.7
3	Oligomer 1	21.6
4	Dimer 2	26.2
5	Oligomer 2	24.2
6	Oligomer 3	22.1
7	Dimer 4	24.2
8	Oligomer 4	23.3

15

Example 6

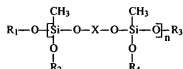
In this Example, 51 g of polycarbonate resin and 9 g of the flame retardant additive of Example 1 were melt blended in a bowl-type mixer at 250°C over a period of five minutes. The resulting flame retarded composition was then compression molded into slabs of 3.0 mm and 1.6 mm thickness. Specimens cut from the 3.0 x 6.0 x 120 mm sized material were used in an LOI test and specimens cut from the 1.6 x 12.5 x 125 mm sized material were used in a for UL 94 flammability. The results are shown in Table 2 against a control formulation not containing the flame retardant.

Table 2

#	Aryl methylsilyl	LOI	UL 94	
			Rating	Dripping
1	None	24.6	Fail	Drips

Claims

1. A fire retarded polycarbonate formulation containing an effective amount of aryl methylsilyl as the flame retardant.
- 5 2. The composition of Claim 1 wherein the polycarbonate is a polycarbonate/thermoplastic resin blend.
3. The composition of Claim 2 wherein the
- 10 polycarbonate/thermoplastic resin blend is a polycarbonate/ABS blend.
4. The composition of Claim 2 wherein the polycarbonate resin is present at a level of 50 - 100 wt. %, more preferably
- 15 at a level 70 - 100 wt. %.
5. The composition of Claim 2 wherein the ABS resin is presented at a level of 0 - 50 wt. %, more preferably at a level 0 - 30 wt. %.
- 20 6. The composition of Claim 1 wherein the fire retardant is an aryl methylsilyl having phenylene bridging groups and having the formula



- 25 where R_1 , R_2 , R_3 , R_4 is aryl or substituted aryl, X is a bridging group derived from a diol and comprising an arylene moiety and n can range from about 1 to about 20.

7. The composition of Claim 1 wherein the aryl methylsilyl is present at a level of 1 - 30 wt.%

ARYL METHYLSILYLS USED AS FLAME RETARDANT ADDITIVESAbstract of the Disclosure

5 A flame retarded resin composition comprising 70-99 wt. %
of a resin comprising 30-100% by weight of an aromatic
polycarbonate resin, and optionally another thermoplastic
resin; 1-30 wt. % of an aryl methylsilyl flame retardant
containing silicon atoms bonded to methyl and phenoxy groups.
This type of composition has a satisfactory flame
10 extinguishing performance and does not produce flammable
drips.